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File: USPT

Jul 29, 1997

DOCUMENT-IDENTIFIER: US 5652193 A
TITLE: Method for hydrocarbon synthesis reactions

ABPL:

A method for producing hydrocarbon synthesis catalyst pellets which include a solid or inert core and a coated layer of porous support impregnated with a catalytic metal, the method provides catalysts which optimize the CO conversion and minimizes selectivity to CH.sub.4.

BSPR:

A metal catalyst (e.g. cobalt or ruthenium) on a support (e.g., titania or silica) which may be promoted by different metals (e.g., rhodium, hafnium and others) are used for synthesis of heavy hydrocarbons from a mixture of carbon monoxide and hydrogen. The principal reaction may be expressed as: ##EQU1## where the distribution of the hydrocarbon products can be approximated by the Flory-Schultz expression. The fraction of oxygenates and olefins in the product is small.

BSPR:

An important consideration in the development of the hydrocarbon synthesis process is to minimize the production of light hydrocarbons (C.sub.1 -C.sub.4), especially of methane. The fraction of methane in the product exceeds that predicted by the Flory-Schultz distribution.

BSPR:

These require the design of catalyst pellets which retain the properties of the powder catalyst (80-140 mesh) but are larger in size (> 1.0 mm). However, since the reactants have to diffuse through liquid-filled pores, the longer diffusion path may create concentration gradients within the pellet. Such gradients alter the hydrogen to carbon monoxide ratio in the pellet due to the lower diffusivity of the latter. As a result the selectivity to methane, which depends on this ratio, increases considerably. Furthermore, since the rate of reaction depends on the concentration of the two reactants, the productivity is smaller in a pellet than in powder.

BSPR:

The present invention is a method for converting hydrogen and carbon monoxide to heavy hydrocarbon in a fixed bed reactor by a catalytic reaction. The method includes contacting the hydrogen and carbon monoxide in the reactor at reaction conditions with a supported catalyst pellet. The support includes an inert or hollow core and an outer layer of porous inorganic refractory oxide. The outer layer has a thickness determined so as to optimize CO conversion to heavy hydrocarbons so that conversion to methane is maintained at a predetermined level. The thickness is-determined by relating the rate of diffusion of the CO and the hydrogen to a rate of reaction in the porous inorganic oxide for a predetermined support geometry, partial pressures, and temperatures. The support may take on many shapes, e.g., sphere, ring or semi-circle.

BSPR:

A metal catalyst (e.g. cobalt or ruthenium) on a support (e.g., titania or silica) promoted by different metals (e.g., rhodium, hafnium and others) are used for synthesis of heavy hydrocarbons from a mixture of carbon monoxide and hydrogen.

BSPR:

The concentrations of both hydrogen and carbon monoxide decrease as they diffuse into the pellet due to significant mass transfer resistance inside the pores. The global rate of CO conversion in the pellet decreases. Furthermore, the methane production rate increases which is a result of its dependency on the ratio between the hydrogen to CO concentration which increases in the pellet. This ratio increases if the parameter γ . (see equation 11 below) is less than unity. This behavior was observed in Co or Ru catalysts supported on titania, silica or alumina.

DEPR:

The two reactants, hydrogen and carbon monoxide, diffuse in the liquid filled pores to reach the active metal sites on the support. The function of the support is to increase the surface area which is equal to about 20 m.sup.2 /g in this

case. At steady-state, the fluxes of the two reactants in the pores are equal (since there is no accumulation):
 ##EQU2## where the flux is expressed as a product of the effective diffusivity $D_{sub,e}$ and the concentration gradient. β is the stoichiometric coefficient which is equal to 2.07 for the hydrocarbon synthesis reaction. The ratio of the gradients depends on the ratio of the two diffusivities. Since the diffusivity of hydrogen is greater than that of carbon monoxide, the hydrogen to carbon monoxide ratio is expected to increase, moving from the pellet surface towards its center.

DEPR:

A differential mass balance inside the pellet pores for the carbon monoxide (which is the limiting reactant, namely it is depleted before the other reactant) yields: ##EQU3## where X is the radial position measured from the external surface toward the center, $\rho_{sub,p}$ is the pellet density $C_{sub,co}$ is the CO concentration in the liquid-filled pores and $r_{sub,co}$ is the intrinsic rate of reaction on the active sites. s is equal to two for a sphere and to unity for a cylinder. This analysis has been carried out for a sphere or a cylinder. However, the analysis can be easily extended to other shapes. For example, rims having a ring shape or a semi-circular shape may be used.

DEPR:

Equation (2) is general for any reaction with diffusion, while the rate of reaction depends on the catalyst system. The intrinsic rate expression (free of internal or external mass transfer resistance) for catalyst systems such as cobalt or ruthenium on titania or silica can be written as: ##EQU5## The values of $k_{sub,1}$, $k_{sub,2}$, $k_{sub,3}$, $E_{sub,1}$, a , b and c are calculated from kinetic rate data obtained in laboratory reactors. The kinetic parameter $k_{sub,1}$ usually depends only on the metal concentration on the support. However, in certain cases such as cobalt on titania, it is also a function of the water partial pressure: ##EQU6## where A is the activity of the catalyst.

DEPR:

Substituting equations (6) and (10) into equation (2) and expressing the equation in dimension-less form yields the dimensionless number ##EQU8## ϕ , called the Thiele modulus, is the ratio between the maximum rate of reaction and the maximum rate of diffusion. If $\phi \gg 1$ the process is diffusion limited while for $\phi \ll 1$ the process is kinetic limited. Since ϕ is directly proportional to the thickness of the active layer or rim, diffusion is important in pellets and negligible in powder. The other factors affecting ϕ are the partial pressures, temperature and the catalyst activity (metal loading).

DEPR:

γ expresses the ratio between the maximum rate of diffusion of the two reactants. If $\gamma = 1$, the ratio of carbon monoxide to hydrogen remains unchanged in the pores while for $\gamma < 1$ this ratio decreases.

DEPR:

Equation (2) is solved to yield the concentration profiles in the pores of the pellet. Then the concentration profiles are integrated over the volume of the pellet to calculate the effectiveness factor which is the ratio of the actual rate of reaction (called the global rate of reaction) and the maximum rate reaction calculated at the surface conditions:
 ##EQU9##

DEPR:

In the experiments with a hydrogen to CO ratio in the feed of less than the stoichiometric ratio (2.07), the ratio decreased along the bed. Since the methane selectivity depends on this ratio, it decreased as the hydrogen to CO ratio decreased. Furthermore, since the diffusion in the catalyst pores was one of the limiting steps in this system, a lower hydrogen to CO ratio increases the parameter γ , which means a lower methane selectivity. A comparison of experiments 4, 5 and 6 illustrates the improvements in methane selectivity. In experiment 3, the methane selectivity increased as compared with experiment, 6 because the temperature was higher. The agreement for both the methane selectivity and the carbon monoxide conversion were good, as shown in Table 2.

CLPR:

1. A method for making a CO hydrogenation catalyst wherein said catalyst includes a metal selected from the group consisting of cobalt and ruthenium deposited in a porous, inorganic, refractory oxide support, said catalyst having said metal located in a rim on the outer surface of said support, said method comprising:

CLPR:

4. The process of claim 1 including applying a promoter material selected from the group consisting of rhenium and hafnium to said rim.